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V.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

A SIMPLE METHOD OF CORRECTING THE WEIGHT OF A BODY FOR THE BUOYANCY OF THE ATMOSPHERE WHEN THE VOLUME IS UNKNOWN.

By Josiah Parsons Cooke.

Presented May 9th, 1883.

It is a familiar fact, that, in the usual method of accurate weighing, the buoyancy of the atmosphere produces a sensible effect, whenever the volume of the load differs materially from that of the equipoise. But, as in all the ordinary processes of chemical analysis, the analyst deals solely with relative weights, the presence of a perfectly dry atmosphere does not influence his results, unless the conditions of temperature and pressure have changed between the successive weighings; and even then the effect is insignificant in most cases. Still, when the volume of the vessel weighed is considerable, differing from that of the weights by as little even as twenty-five cubic centimeters (for example, in weighing the absorption tubes used in "organic analysis"), the error caused by variations in the density of the atmosphere may be sufficient seriously to impair the accuracy of the result.

In weighing large vessels — as in determining the density of a gas — the effect of any variation of buoyancy is eliminated by the well-known methods of calculating the results; but the formulas usually given for that purpose involve as known quantities the volume of the vessel, the volume of the weights, the density of the air under the standard conditions, as well as the temperature and pressure at the time of the several observations; and, since the calculations are somewhat complex, and the required data not always readily obtained, the formulas are seldom applied unless the volume of the load is quite large. Moreover, in these formulas the effect of each factor cannot readily be traced, and most analysts are probably not aware of the extent to which their weighings may be influenced by changes in the density of the air due to variations of temperature and pressure. In seeking to fix the weights of certain absorption tubes, (in connection with my work on the revision of the atomic weights,) I have been led to a method of correcting the weights of such tubes for variations of buoyancy; which, while it does not involve the determination of any data except the temperature and tension of the air in the balance-case, and is as simple in its application as the calibration of a flask, also gives a clear conception of the effect of each variable on the weight.

It is assumed that the air of the balance-case is dry; and with one of Becker's balances I have not been able to trace any effect on the weight of a glass vessel from variations of hygrometric condition, when two open dishes of sulphuric acid (three inches in diameter) were kept in the case, which has a volume of about thirty-seven cubic decimeters. Under such circumstances, the only causes which sensibly modify the weight of a small glass vessel (like a closed potash bulb-tube) are the variations of temperature and pressure. The relative effect of these two variables will appear from the following considerations, which suggested the method I am to describe.

If we assume thirty inches of mercury as the standard of barometric pressure, it is obvious that the variation of each tenth of an inch from this standard will determine a change of $\frac{1}{300}$ in the resultant effect of the buoyancy of the air on the load and its equipoise. Again, if we assume 27° C. as our standard of temperature, — that is, 300° on the so-called "absolute scale," — then, according to the law of Charles, the variation of each degree from this point will also cause a change of $\frac{1}{300}$ in the same resultant. In other words, counting from these standards, a variation of one degree in the Centigrade thermometer indicates the same effect on the density of the air, and therefore on its buoyancy, as the change of $\frac{1}{10}$ of an inch in the mercurial barometer. In our climate the barometer changes slowly, and its fluctuations do not ordinarily exceed one inch. On the other hand, the balances in our chemical laboratories are liable to rapid changes of temperature, which often exceed twenty degrees, the equivalent of two inches. Hence, of the two variables the temperature is by far the more important.

If we select the two standards of temperature and tension here assumed, we can easily correct for temperature by simply adding to the observed height of the barometer (in tenths of an inch) the difference between 27° C. and the temperature observed. — Of course the correction becomes negative if the temperature exceeds

27° C.— Having thus eliminated the effect of temperature, we can (after taking a few weighings under as great a variation of temperature and pressure as we can command) easily find the difference of weight which corresponds to a variation of $\frac{1}{10}$ of an inch in the barometer, and we thus obtain a constant for the vessel (or other object weighed) by means of which we can rapidly reduce the weights obtained to the standard of thirty inches' barometric pressure, having previously reduced them to the standard of 27° C. for temperature. The weights, having now been corrected for buoyancy, can be compared; and, although the standards assumed may be as unusual in their association as is one of them in its value, they are as legitimate as any others, and will be found in practice more convenient.

To apply this method of reduction we simply leave the load equipoised on the balance, shifting the rider with the varying weight, and noting the corresponding temperatures and pressures, until a sufficient difference has been observed; and a difference corresponding to 20° C., or two inches of mercury, is adequate in most cases. The process corresponds to calibrating a flask, and the constant, once obtained, can be afterwards used for the same vessel, unless the weight of its contents is materially altered. The following examples will show the application of the method.

In each case the load was a closed absorption tube of peculiarly irregular construction, but not much larger in volume than those generally used in organic analysis. We give in the accompanying tables, first, the date; secondly, the observed weight; thirdly, the temperature of the balance-case; and, fourthly, the height of the barometer at the time of weighing in tenths of an inch. These are the observed data. In the fifth column we give the reduced heights of the barometer for 27° C., and these values are obtained by simply subtracting the observed temperatures from 27°, and adding the remainders to the observed barometric heights. Below the table we print in each case the largest weight observed over the smallest weight observed, and on the same lines the corresponding reduced barometric heights. Dividing now the difference of weight in milligrammes by the difference of height in tenths of an inch, we obtain the value last given, which we have called the "constant." With this constant we can very rapidly reduce all the weights to the common standard of thirty inches, and this we do by multiplying the difference between 300 and the reduced barometric heights by this constant, and adding or subtracting the product, as the case may be, to or from the observed weights.

TABLE OF WEIGHTS.

First Series.

No.	1883.	Weight.	C.°	H.	H. reduced.	Result.
			°			
1	May 1	87.5304	17	304.0	314.0	87.5346
2	" 2	87.5303	17	304.2	314.2	87.5346
3	" 2	87.5314	19.5	303.2	310.7	87.5346
4	" 3	87.5322	20	301.0	308.0	87.5346
5	" 4	87.53205	20.5	301.9	308.4	87.5346
6	" 4	87.5320	21	302.5	308.5	87.5346
7	" 6	87.5316	18	300.8	309.8	87.5345
8	" 7	87.5320	19	300.0	308.0	87.5344
9	" 8	87.5328	19.5	298.9	306.4	87.5347
10	" 9	87.53245	22	302.2	307.2	87.5346
11	" 11	87.5333	22	299.5	304.5	87.5346
12	" 11	87.5333	19.5	296.2	303.7	87.5344
13	" 19	87.5317	21	303.5	309.5	87.5346
14	" 21	87.5345	23	296.2	300.2	87.5346
15	" 22	87.5336	22	298.0	303.0	87.5345

Greatest weight,	87.5345	Barometer,	300.2
Smallest weight,	87.5303	"	314.2
Differences,	42		14.0

Constant = 4.2 mg. ÷ 14.0 = 0.3 mg.

The balance here used is only sensitive under such a load to the tenth of a milligramme, and hence the constancy of the results obtained is very striking. There can be no question that the mean of the several weighings is accurate to the full limit of the sensibility of the instrument used. Moreover, during the course of the observations it was also evident that the slight variations observed (only $\frac{3}{10}$ of a milligramme between the extreme limits) were owing to the want of exactness in the measure of temperature of the balance-case. We used a common thermometer reading only to whole Centigrade degrees; although, as afterwards appeared, a difference of only $\frac{3}{10}$ of a degree caused a variation of $\frac{1}{10}$ of a milligramme in the weight, and a difference of a whole degree corresponded to the extreme difference between the observations. In the Second Series (made with the same tube, but differently mounted) we used a standard thermometer (Geisler's make) reading to tenths of a degree, and the results are all that could be expected with the instruments employed. The observations were made, nevertheless, under the most unfavorable conditions, during exceedingly hot weather, when the temperature was rapidly changing;

and it was evident that the insignificant differences remaining arose from the circumstance that the thermometer was not nearly so sensitive as the air in the balance-case, following the changes of temperature of the air after a considerable lapse of time. It was curious to notice the slight increase of weight, caused by the radiation of the body while weighing, followed after some time by a rise of the very sensitive thermometer employed; and this effect was obtained with a displacement of only about 75 cubic centimeters of air.

TABLE OF WEIGHTS.

Second Series.

No.	1883.	Weight.	C.°	H.	H. reduced.	Result.
1	May 29	87.3447	° 23.5	297.6	301.1	87.3451
2	" 30	87.3432	23.2	302.0	305.8	87.3451
3	" 30	87.3437	24.5	301.8	304.3	87.3451
4	" 31	87.3444	23.8	298.8	302.0	87.3450
5	June 1	87.3429	22.8	302.4	306.6	87.3450
6	" 1	87.3432	23.75	302.4	305.65	87.3450
7	" 2	87.3419	22.6	305.2	309.6	87.3451
8	" 3	87.3420	21.95	304.5	309.55	87.3450
9	" 3	87.3427	23.15	303.8	307.6	87.3451
10	" 4	87.3441	25.0	301.1	303.1	87.3451
11	" 5	87.3443	26.0	301.4	302.4	87.3451
12	" 5	87.3446	26.3	300.6	301.3	87.3450
13	" 6	87.34435	25.55	300.75	302.2	87.3451
14	" 7	87.3452	26.7	299.0	299.3	87.3450
15	" 8	87.3464	29.4	297.9	295.5	87.3450

Greatest weight,	87.3464	Barometer,	295.5
Smallest weight,	87.3419	"	309.6
Differences,	45		14.1

Constant = 4.5 mg. ÷ 14.1 = 0.319 mg.

NOTE. — In combining only the extreme weights, we must obviously take care that neither of them is seriously affected by any accidental errors; and a more certain value of the constant would be obtained by combining all the observations after well-known methods. This complication, however, is seldom necessary; as such errors would render the final result irregular, and lead to a rediscussion of the observations.

The limits in the accuracy of the method here described are obvious; but it will be noticed that the accuracy of the method is exactly proportional to the requirements. The greater the volume of the load, and hence the greater the effect of buoyancy, the more accurately can the "constant" be found, by which the correction required in any case can be calculated; and, as the above examples abundantly prove, the accuracy is sufficient for the purpose in view. When the volume of the load is large, it becomes necessary to measure the temperature and pressure with great precision, and to protect the balance from radiation, and from all causes of rapid change of temperature. It was a great satisfaction to the author to find that by so simple means the relative weight of glass vessels of considerable size may be determined with accuracy to the tenth of a milligramme, — an accuracy which is fully equal to that of the most refined processes of chemical analysis.

From the data given, and from the known normal density of the air, it can easily be calculated that in the first series of weighings the volume of the tube and mountings exceeded that of the weights by about 75 cubic centimeters. With this difference of volume we have a variation of $\frac{3}{10}$ of a milligramme of weight for a difference of $\frac{1}{10}$ of an inch of mercury in tension, or one degree in temperature. Hence, with a difference of volume of 100 cubic centimeters, we should have a variation of weight amounting to about four milligrammes for every difference of one inch in the barometer, or of ten degrees of the Centigrade thermometer; and these data will furnish the basis for a rude estimate of the effect in any given case. If the difference of volume amounts to 2,500 cubic centimeters, then a difference of $\frac{1}{1000}$ of an inch in the barometer, or of $\frac{1}{100}$ of a degree in the thermometer, would cause a variation of $\frac{1}{10}$ of a milligramme in the weight; so, also, a variation in the intensity of gravity amounting to only $\frac{1}{30000}$ of the whole amount would produce a similar effect, and a sensible variation would follow any marked change in the purity of the air. Hence, the balance might be used to detect exceedingly minute changes in any one of these variables, provided the others could be exactly controlled; and although with our better methods these applications of the balance may be of no practical value, yet the considerations here adduced will serve to show how sensitive the instrument is to the slightest changes in the density of the air when loaded with vessels of large volume. The best method of controlling the weight in such cases is that adopted by Regnault in his classical work on the density of the more permanent gases. This consists in balancing the vessel whose contents are to be weighed with a second vessel of equal volume, the two hanging side by side in a case lined with thick felt. The balance is set over the case, and the vessels are suspended from the pans by means of platinum wires, which swing freely through holes made in the base of the instrument.